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A RADIOIODINE DETECTOR BASED ON LASER INDUCED FLUORESCENCE. (U)

MAY 77 A P BARONAVSKI; J R McDONALD

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A Radioiodine Detector Based on Laser Induced Fluorescence

A. P. BARONAVSKI and J. R. McDONALD

*Chemical Diagnostics Branch
Chemistry Division*

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20. Abstract (Continued)

under flowing conditions, and ultimate sensitivities are discussed. An evaluation of the technique and extension to a portable, real time monitoring instrument for use in the field is given.



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A RADIOIODINE DETECTOR BASED ON LASER INDUCED FLUORESCENCE

1.0 INTRODUCTION

1.1 Needs and Applications for Radioiodine Monitoring

Of the six major iodine isotopes produced in nuclear reactors, ^{129}I represents only about 1% of the main fission product iodine isotope yield.¹ Although this isotope has the lowest specific activity and the lowest energy decay products, after a few days of cooling outside the reactor the major iodine isotope present is ^{129}I , because the next longest-lived isotope ^{131}I has a decay half-life of 8.0 days. In view of the very long ^{129}I half-life of about 17 million years new attention has been directed to its cumulative effects.^{2,3} In spent fuel processing ^{129}I will have to be recovered and stored indefinitely because of its longevity. Because of the low specific activity, low energy decay products, and because ^{129}I is a minor iodine isotopic constituent in an active core its detection by counting techniques is often slow and impractical.

Activated charcoal is the most widely used material employed for iodine removal and it is also used as a means for decay storage. Because organic compounds of iodine are adsorbed less well than I_2 on activated charcoal substrates, in some applications charcoals are used which have been impregnated with substances which react chemically with I_2 and compounds of iodine or which undergo an isotopic exchange.¹ Among examples currently used are charcoals impregnated with KI (or other inorganic iodine compounds) in which the stable isotope of the impregnant iodine can undergo an exchange (or reaction) with the radioiodine. Note that such an exchange can release a stable iodine into the effluent.¹ The efficiency of charcoal filters is strongly dependent upon their environmental history, (particularly extended exposure to very high relative humidity)⁴ and the desorption rate of iodine from the filters is strongly dependent upon temperature.⁵ It appears that

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there exists a need to monitor and measure quantitatively in real time, iodine concentrations in several areas:

- (a) as a continuous monitor to observe breakthrough behind critical filter facilities;
- (b) as a testing and trouble shooting field measuring tool to test the integrity of in place filters;
- (c) as a monitor of fairly high ^{129}I ambient concentrations in spent fuel reprocessing and;
- (d) as a monitor to observe accidental large releases of radio-iodine in the spent fuel reprocessing cycle.

1.2 Proposed Research

For the reasons outlined above NRL in cooperation with ERDA (Oak Ridge Operations Office) has contracted to design and laboratory test an instrument for the detection of low concentrations of ^{129}I , in ambient atmospheres. The proposed instrument is to be based upon a laser induced fluorescence technique. In the design and evaluation of the proposed instrument the following characteristics were to be stressed:

- (a) the specified final instrument must be easily portable and capable of use under field conditions;
- (b) the instrument should be specific for ^{129}I ;
- (c) the specified instrument should be capable of making real time measures - preferably on flowing gas samples;
- (d) the final field hardened instrument should be capable of continuous operation over extended periods of operation and;
- (e) the instrument should be as sensitive as possible consistent with an economic appeal which would allow widespread use in the industry of the field instrument.

During the first year of research on design of the laser-fluorescence instrument it was proposed to:

- (a) test the feasibility of the laser technique;
- (b) construct a breadboard designed detector;

- (c) measure the limits of sensitivity for detection of $^{129}\text{I}_2$ under evacuated conditions and at one atmosphere of air;
- (d) evaluate possible chemical interferences involved in the technique;
- (e) evaluate the feasibility of a ^{129}I diagnostic instrument based upon the results of laboratory tests and;
- (f) if favorable, specify the characteristics of the field instrument to be designed.

As significant progress has been made toward the goals of the first years research, this interim report is being prepared to aid in decisions which must be made concerning taking the next step of construction of prototype instruments for evaluation purposes in the field.

2.0 EXPERIMENTAL

2.1 Approach to Experimental Problem

A laser induced fluorescence technique was chosen for application to monitoring of I_2 concentrations. In this technique a laser photon of appropriate frequency impinging upon the sample is selectively absorbed by the iodine molecule placing it in a metastable excited electronic state. The excited iodine molecule can relax by collisional processes back to the ground state in which case it will not be detected, or it may relax by reemitting a photon (of longer wavelength) by a fluorescence mechanism. This fluorescence emission may be detected by a photoelectric detector. The resulting fluorescence signal, after appropriate corrections are made for competing collisional relaxation processes, collector efficiency, detector response characteristics, and other emissive interferences, can be used to determine the I_2 concentrations in a gas sample. Several problems which must be considered in the application of this technique to quantitative measurements are enumerated below:

- (a) a laser excitation frequency must be chosen which corresponds to an optical resonance of the specific molecule to be detected;

(b) excitation frequencies must be selected which do not correspond to resonances of other species in the sample (i.e. other I_2 isotopes);

(c) evaluation must be made of all non-fluorescing deactivation pathways which the selected molecule may undergo;

(d) possible fluorescing interferences from other species must be accounted for;

(e) allowance must be made for all possible molecular forms in which the atom to be detected may occur and appropriate corrections be made.

2.2 Spectroscopic Considerations

The I_2 molecule has a very characteristic absorption in the visible region of the spectrum. The major absorption features and the electronic transition assignment have been known for many years^{6,7} for the red band system. The transition is a spin forbidden process $\tilde{B} (^3\Pi_{Out}) \leftarrow \tilde{X} (^1\Sigma_g^+)$ which is made relatively allowed by the heavy atom nature of the atoms involved. The visible band fluorescence of this system was first critically evaluated over 70 years ago.⁸ Scores of studies of both absorption and emission have been carried out in the intervening years. Recently the absorption lines in this transition have been chosen to use as a new secondary wavelength standard by workers at the National Bureau of Standards. For this application it has been necessary to catalogue very precisely many of the absorption features of this spectrum. Hanes and Dahlstrom,⁹ Walland¹⁰ and Hanes et al.,¹¹ have frequency stabilized a $^3\text{He}-^{20}\text{Ne}$ laser to hyperfine components in the absorption spectrum of $^{127}\text{I}_2$ at 633 nm and Knox and Pao¹² have frequency stabilized a $^3\text{He}-^{20}\text{Ne}$ laser to hyperfine components in the $^{129}\text{I}_2$ spectrum near 633 nm. More recently Schweitzer,¹³ et al. have carried out similar work using a $^3\text{He}-^{22}\text{Ne}$ laser monitoring resonances of $^{129}\text{I}_2$. It was shown in the latter work that the gain curve of the $^3\text{He}-^{22}\text{Ne}$ laser overlaps ~20 hyperfine components in the $^{129}\text{I}_2$ spectrum, but does not have any interferences from absorption features of the more common isotope $^{127}\text{I}_2$.

For the above reasons the ^3He - ^{22}Ne laser was chosen as the preferred excitation source for the laser induced fluorescence experiments on I_2 .

2.3 Equipment Design

3.3.1 $^{129}\text{I}_2$ and ^{22}Ne Spectral Characteristics

In Figure 1 a portion of the spectrum of $^{129}\text{I}_2$ in the region of the ^{22}Ne gain curve is shown. These spectral lines are shown as measured by Lamb Dip spectroscopy and are not pressure or Doppler Broadened. The wavelength of the B feature is 6329.90\AA . The B feature is separated from the A feature by $\sim 0.003\text{\AA}$. In experiments such as those conducted in this work the Doppler and pressure broadening of the features shown in Figure 1 will merge all these hyperfine components into an apparent continuum absorption as represented schematically by the dashed curve immediately above the stick spectrum. A schematic of the gain curve of the ^{22}Ne laser is shown immediately above the dashed curve as a solid line. A ^{22}Ne laser oscillating between two cavity mirrors can lase upon a selected frequency or frequencies anywhere on this gain curve. The actual operating characteristics (bandwidth, number of cavity modes operating and mode spacing) of an individual He-Ne laser will depend upon gas fill pressure, gas mix, discharge current and cavity length of the laser employed.

2.3.2 Specifications of ^3He - ^{22}Ne Laser

The laser purchased for this is a basic Jodon Model HN-7 configured for TEM_{00} operation at 6328\AA . A special fill of ^{22}Ne was specified for the laser. The power output of the laser upon arrival was 16.0 mwatt, a value which has held constant over several months of operation. The spectral characteristics of the laser were measured with a Coherent Optics Model 380 Interferometer. We find that there are five to six cavity modes oscillating at all times. The oscillation of these cavity modes with their characteristic 260 MHz cavity spacing is indicated schematically superimposed upon the laser gain

curve shown in Figure 1. Since the Doppler width of the I_2 resonances is ~ 200 MHz any frequency jitter in the ^{22}Ne laser frequencies is not reflected in the absorption efficiency of the pseudo continuous absorption of $^{129}\text{I}_2$ across the whole ^{22}Ne laser gain curve.

2.3.3 Fluorescence Cells and Photomultiplier Detection

The fluorescence cells used for static measurements are constructed of quartz and are 1 inch cubes. The scattered laser light is rejected by combinations of corning glass long wavelength pass sharp cut filters and specially constructed dielectric blocking filters. The 6328\AA laser light is rejected and all fluorescence of $\lambda \gtrsim 6600\text{\AA}$ is detected. The detector is an RCA 31000A 2" photocathode extended S-20 response photomultiplier. A block diagram of the breadboard detector is shown in Figure 2.

2.3.4 $^{129}\text{I}_2$ Samples and Pressure Control

In order to generate a set of working curves it is necessary to make static measurements on known pressures of $^{129}\text{I}_2$. The $^{129}\text{I}_2$ samples were obtained commercially from ICN Inc. in sealed ampules each containing 3 mg of $^{129}\text{I}_2$. The samples were introduced into the fluorescence cells on a vacuum line and then sealed off. The $^{129}\text{I}_2$ pressure is controlled in the static cells by means of constant temperature slush baths. I_2 vapor pressure curves as a function of temperature were taken from the International Critical Tables. Various constant temperature slush baths were employed to control the temperature between -55 and 0°C . In addition, various measured temperature baths were produced with ice- $\text{NaCl-H}_2\text{O}$ mixtures. A Table of convenient slush baths with corresponding temperatures and I_2 pressures is shown in Table I.

Table I

<u>Compounds</u>	<u>Slush Temperature</u>	<u>I₂ Pressure (mtorr)</u>
H ₂ O (ice)	0°C	31
H ₂ O (ice) + NaCl	0°, -14°C	31 - 7.0
CCl ₄	-22.5°C	2.6
Chlorobenzene	-47°C (-45.2°C)	0.13
Chloroform (CHCl ₃)	-53°C	.035
N ₂ (liquid)	-196°C	~0

2.3.5 Fluorescence Signal Detection and Processing

Because of the ease of operation and availability of equipment it was decided to measure fluorescence signals by means of lockin amplifier detection. It should be possible to obtain equivalent results by photon counting techniques. The lock in amplifier employed is a PAR Model HR-8 used with the appropriate chopper and chopper reference. Because of small, but finite scattered laser light signals, we have found it convenient to employ a PAR Model 123 A.C. zero offset to null out the scattered laser light signal when measuring low level signals. Using this nulling device one can easily zero out scattered laser light down to $< 10 \mu\text{volts}$ full scale thus extending the sensitivity by \sim a factor of a hundred.

The photomultiplier signal is also monitored by an oscilloscope which is convenient for monitoring the signal level at relatively high I₂ pressures for purposes of monitoring photomultiplier dark current levels and for aligning the laser and fluorescence cells, etc.

2.3.6 Notes on Handling ¹²⁹I₂ in Static Cells

During the course of this work we have noted a deterioration of fluorescence signals from our ¹²⁹I₂ reference cells on several occasions. These problems were tracked down to a H₂O contamination problem. I₂ reference samples which have been exposed to a trace

contamination of H_2O have much different vapor pressure characteristics than when completely dry. The introduction of one atmosphere of moist laboratory air is sufficient to form a surface layer coating over the I_2 samples which is visible to the eye. Resublimation of these samples does not allow one to recover the samples effectively. In all cases contaminated samples of I_2 give significantly lower equilibrium vapor pressure of I_2 than do the pure samples. We have been able to introduce dry air into the fluorescence cells and subsequently reclaim the I_2 reference samples if one uses clean vacuum techniques and carefully handles the samples. I_2 samples for reference cell purposes are best prepared under dry high vacuum techniques and should be permanently sealed off.

3.0 RESULTS

3.1 Static Measurement

3.1.1 Single Component Gases

Using the detector design shown in Figure 2, $^{129}\text{I}_2$ fluorescence signals were measured from two different fluorescence cells for two separate samples of $^{129}\text{I}_2$ over many repetitions at various temperatures in cells containing only $^{129}\text{I}_2$. Apparent pressure equilibrium is obtained after ~ten minutes with a new temperature slush bath. Before and after each series of measurements the sample is frozen out at 77°K to check the background correction factor. The upper curve in Figure 3 shows a plot of fluorescence signal intensity as a function of $^{129}\text{I}_2$ pressure (and concentration). Measurements have been made over iodine concentrations between 5×10^{-7} and 4×10^{-10} g/cm³. A good straight line signal response is obtained over this range. For the lower concentration measurements the ability to measure signals is not limited by the fluorescence signal, but by the uncertainty in the known vapor pressure curves of I_2 as a function of temperature. The practical limits of sensitivity for fluorescence measurements are indicated by the dotted line extension of this curve. Since the signals follow a

linear response curve it is possible to measure in evacuated systems I_2 concentrations to near one picogram per cm^3 .³ The working curve so obtained is in no way dependent upon a need to independently measure the absolute I_2 concentration by vapor pressure curves or other techniques below the 10^{-10} g/ cm^3 level.

3.1.2 Multicomponent Gas Mixtures

Working fluorescence signal curves were also obtained for $^{129}I_2$ in the presence of a rare gas buffer and in the presence of air. Since bimolecular quenching of I_2 fluorescence is a well documented process, the loss of fluorescence signal in the presence of other gases is predictable.¹⁴ However, since the quenching process is dependent upon the pressure, the collision partner, and the excitation wavelength, independent measurements are required for this new experimental setup. As it is anticipated that measurements will be made with this detection system only under either evacuated conditions or in the presence of one atmosphere of air or some other buffer gas, multicomponent gas mixtures were measured only at one atmosphere total pressure. The middle curve in Figure 3 shows a plot of I_2 fluorescence signal as a function of I_2 concentration in the presence of one atmosphere of Argon while the lower curve is in the presence of one atmosphere of air. In the presence of Argon the fluorescence signals are decreased by a factor of 86.0 while in air the signals are decreased by a factor of 131.7 over the respective values under evacuated conditions. The quenching cross sections for He, Ar, N_2 , O_2 and CO_2 from Capelle and Broida¹⁴ are given in Table II for excitation at 6234 Å. The relative fluorescence efficiencies observed in this work are in essential agreement with what is expected based upon the relative quenching efficiencies of the gases in Table II. It is apparent that there is little advantage to be gained from scrubbing I_2 from the air and rediluting it in an Argon carrier gas. On the other hand the data in Table II indicate that one might gain a factor of ten to twenty in increased sensitivity if one were to make measurements in one atmosphere of He gas as opposed to air.

Table II

<u>Quenching Gas</u>	<u>Cross Sections</u> (in 10^{-16} cm^2)
He	0.44 ± 0.26
Ar	5.62 ± 0.24
N ₂	5.0 ± 0.6
O ₂	7.8 ± 0.3
CO ₂	22.1 ± 0.9

With the equipment as presently set up it is feasible to measure $^{129}\text{I}_2$ concentrations at atmospheric pressure (air) to concentration levels at or below 10^{-10} g/cm^3 . As this limit of sensitivity appears to be in the range required for applications of the proposed instrument the specified equipment design will be built around measurements to be made in ambient air. This will simplify the design of the final instrument and will avoid the requirement for scrubbing I_2 and rediluting it into inert carrier gases. It will also avoid the possible pitfalls resulting from the tendency of I_2 to plate out and hang up on otherwise clean surfaces.

3.2 Measurements Under Flowing Conditions

At the present time we have not extended our measurements to flowing cells. To make laboratory measurements under these conditions will require:

- (a) A much larger inventory of radioactive $^{129}\text{I}_2$ than used in the static experiments;
- (b) glassware, gas metering, and flow measuring equipment;
- (c) construction of flowing gas cells and;
- (d) an independent means of measuring the $^{129}\text{I}_2$ effluent from our experiments.

Such measurements are to be desired for several reasons:

(a) The measurements will demonstrate that the technique can be transferred from measurements under static conditions to a performance level which will be required in the field;

(b) an independent crosscheck can be made between this technique and a wet chemical analysis technique currently used in our laboratories;⁵

(c) the proposed monitor can be evaluated against radiocounting analysis and;

(d) laboratory procedures need to be developed for use in evaluating prototype fluorescence detection instruments to be acquired.

For these reasons it is desirable that the present breadboard equipment be redesigned to accommodate flowing measurements.

4.0 EVALUATION OF THE LASER FLUORESCENCE TECHNIQUE

4.1 Applications and Limits of Sensitivity

Laboratory measurements with the breadboard detector clearly demonstrate that an $^{129}\text{I}_2$ monitor based upon the laser fluorescence technique will be a sensitive, practical and relatively inexpensive field monitoring instrument for $^{129}\text{I}_2$ measurements down to or below the one hundred picogram/cm³ level. Such an instrument will be capable of real time instantaneous measurements or capable of operating in an integrating mode to give accumulation loads over a period of time. The components of the prototype instruments should be capable of continuous operation over many thousands of hours for use as a monitoring device. The field and prototype models will be essentially self-contained and readily portable for use in the field checking the integrity of power plant charcoal filters. The dynamic concentration range of the prototype and field instruments should be in excess of 10^5 and if required and specified will be capable of measurements over a range of 10^8 , i.e. up to $\sim 10^{-2}$ g/cm³ of $^{129}\text{I}_2$.

4.2 Interferences and Isotopic Scrambling

Measurements have been made with the breadboard detector for sensitivity using samples of $^{127}\text{I}_2$. The signals measured indicate that $^{127}\text{I}_2$ is detected with a sensitivity of less than 1% that of $^{129}\text{I}_2$. It is unclear at this point whether fluorescence signals from $^{127}\text{I}_2$ result from excitation by the plasma discharge light in the He-Ne laser or whether there exist very weak unmeasured $^{127}\text{I}_2$ resonances in the region of the laser gain curve. These determinations can be made if the need warrants it.

If a very large excess of $^{127}\text{I}_2$ over $^{129}\text{I}_2$ is present in the effluent gas to be measured a significant portion of the ^{129}I present will be tied up in the mixed isomer molecule $^{127}\text{I} - ^{129}\text{I}$. Our detection sensitivity for this molecule and other mixed isomer molecules is undetermined. These measurements can also be undertaken if it is apparent that they are needed in the particular application required.

It has been pointed out that a portion of the iodine present, particularly downstream from charcoal filter beds, is in the form of alkyl iodides, (CH_3I , $\text{C}_2\text{H}_5\text{I}$, etc.). The laser fluorescence technique developed herein is completely insensitive to ^{129}I in any organic form. Work underway at NRL¹⁵ on a catalytic pyrolyzer has shown the capability of conversion of organic iodides to molecular iodine. If such a device is required its inclusion immediately prior to the gas intake of the laser fluorescence detector can be provided for. This instrument should also serve to strip I_2 adsorbed on the surface of any particulate matter in gas stream to be detected.

4.3 Specification of Prototype Instrument

At this point laboratory studies have made it possible to specify many of the desirable design features which should go into the construction of the prototypes for $^{129}\text{I}_2$ field monitors. A schematic block diagram of the proposed prototype detector is shown in Figure 4. The prototype instruments will necessarily contain a reference sample of

$^{129}\text{I}_2$ which will be used to ratio against the unknown samples to be measured. In this way small variations in the laser power or alignment of components will not effect the accuracy of measurements. The detection is shown schematically as based on a lockin amplifier. It may be desirable to use photon counting techniques. This is an evaluation which will have to be made based, in part, on economic considerations and physical space constraints. It may also be desirable to modulate the excitation laser rather than use mechanical choppers. It is likely that the final design instrument will contain microprocessing circuitry to allow automatic sensitivity changes to be made and to supply digital readout and integrated sample loadings. The prototype instrument should also allow for some internal reference measurements (i.e. laser power, absolute reference signal intensity, background signal nulling, etc.) to aid in field adjustment and trouble shooting. It is anticipated that the prototype system will be of a ruggedized and modular design which will allow for ease of portability and operation. The only external connections which should be required will be a standard 110V ac power outlet.

4.4 Other Design Options

It should be noted that several options are feasible for incorporation into a laser fluorescence iodine monitor. The present studies have been built around an assumed need to specifically measure $^{129}\text{I}_2$. By changing the specifications of the excitation laser it is possible to build a detector which will detect essentially the sum of all isotopic I_2 species. Such a detector would not be specific for $^{129}\text{I}_2$, but if used in conjunction with the detector specified in this work it would be possible to detect both $^{129}\text{I}_2$ and total I_2 .

If a requirement becomes apparent to measure much lower concentrations of $^{129}\text{I}_2$ than is feasible with the present detector it should be possible to extend the limits of sensitivity of the proposed instrument by using I_2 scrubbing techniques for larger samples of air followed

by measurement of $^{129}\text{I}_2$ in a carrier flow of helium. It would likely be possible to extend the sensitivity limits by several factors of 10 for the proposed instrument.

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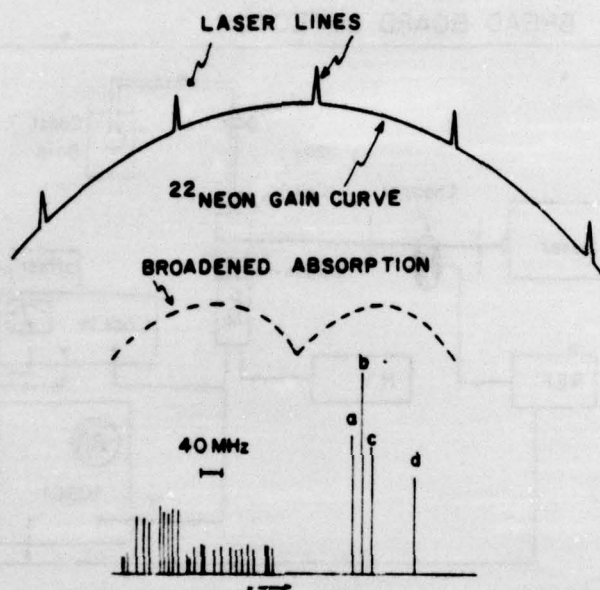


Fig. 1 — Spectroscopic characteristics of the $^{129}\text{I}_2$ spectrum and the $^3\text{He}\text{-}^{22}\text{Ne}$ laser. The line spectrum at the bottom is the hyperfine absorption spectrum of $^{129}\text{I}_2$ measured by Lamb Dip spectroscopy from Ref. 13. The dashed curve above this represents the Doppler and pressure broadened absorption of $^{129}\text{I}_2$ characteristic of ambient temperature and pressure conditions. The solid curve at the top schematically represents the $^3\text{He}\text{-}^{22}\text{Ne}$ laser gain curve while the spikes on this curve schematically represent five oscillating modes characteristic of the laser employed in this work.

BREAD BOARD DETECTOR

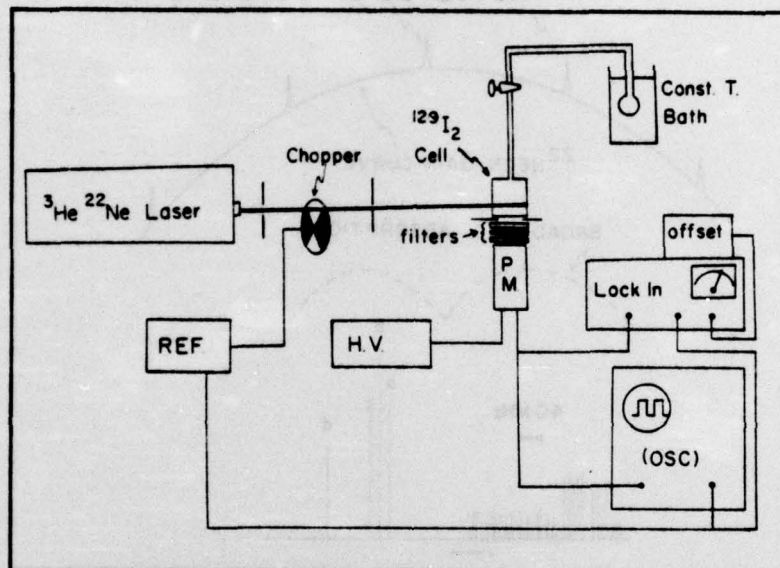


Fig. 2 — Schematic representation of the breadboard detector employed in this work

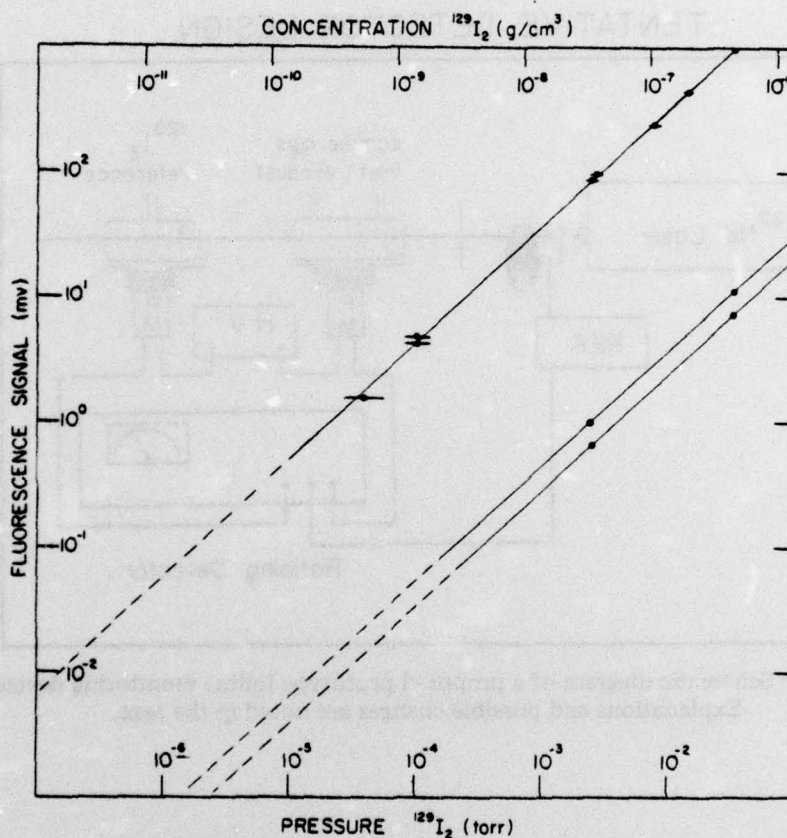


Fig. 3 — Working curves for $^{129}\text{I}_2$ fluorescence intensity as a function of pressure or concentration. The upper curve is measured for $^{129}\text{I}_2$ in evacuated static cells. The horizontal error bars represent the uncertainty in the I_2 pressure resulting from uncertainty in the absolute temperature-vapor pressure measurements for I_2 . The vertical error bars are smaller than the size of the dots in the figure, i.e. $\sim \pm 10 \mu\text{volts}$. The center and lower curves are fluorescence signal response for $^{129}\text{I}_2$ in a static cell in the presence of 1 atm of argon and 1 atm of air respectively.

TENTATIVE DETECTOR DESIGN

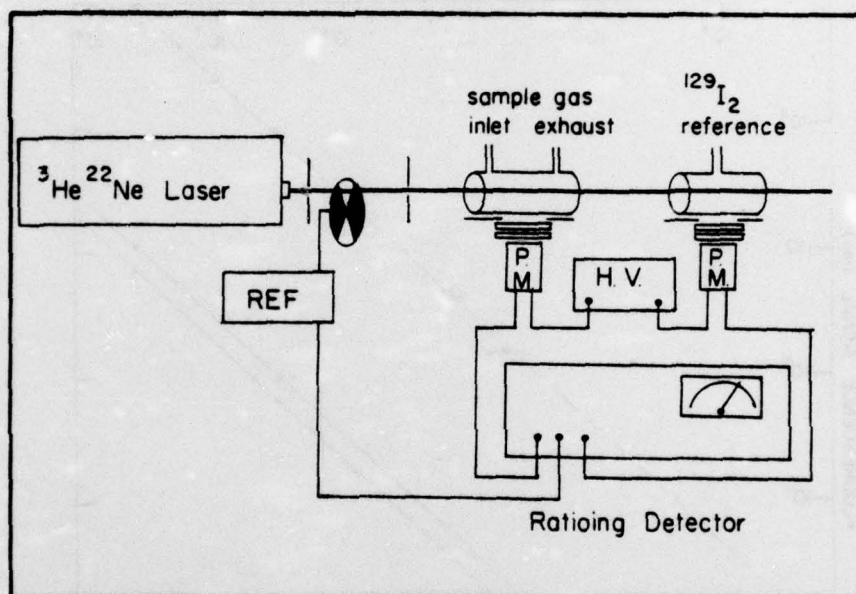


Fig. 4 — Schematic diagram of a proposed prototype iodine monitoring device.
Explanations and possible changes are noted in the text.